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INFORMATION CIRCULAR

DEPARTMENT OF COMMERCE -- BUREAU OF MINES

GRAPHITE

PART III - UTILIZATION OF GRAPHITE

BY

PAUL M. TYLER

Circular No. 6123
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PART III. UTILIZATION OF GRAPHITE[1]

By Paul M. Tyler[2]

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INTRODUCTION

The outstanding trend in the graphite market is the fast-growing demand for cheaper qualities of graphite and the declining consumption of the more expensive varieties. The manufacture of graphite crucibles for melting metals was one of the earliest applications of the mineral and for many years constituted by far the leading source of demand. In later years, however, and more especially since the Great War, the increasing demand for high-grade steel ingots and castings instead of enlarging crucible sales has permanently curtailed the domestic demand for crucibles because it has hastened the introduction of electric, oil or gas fired furnaces to replace the older types requiring pots to hold the metal during melting. While there has been a substantial increase in the use of graphite for miscellaneous refractories the total consumption for such purposes is too small to offset the shrinkage in demand for crucible making, and though it consumes the better and hence more expensive grades of crystalline flake graphite, it does not call so insistently for the still costlier Ceylon grades.

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1 - The Bureau of Mines will welcome reprinting of this article but requests that the following footnote acknowledgment be made: "Printed by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)"

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CONSUMPTION OF GRAPHITE BY VARIOUS INDUSTRIES

The relative importance of the various outlets for both natural and artificial graphite is indicated by the results of the canvass made by the U. S. Tariff Commission of actual sales to ultimate consumers in the years 1923 and 1924. These figures fail to reveal the large quantities of graphite consumed in dry batteries, and probably there have been subsequent minor changes in the standing of the various consuming industries; but nevertheless these data are by far the most complete that have ever been made available. In fact, it is the first attempt to make a census of all consumers. Previous estimates have all represented merely guesses made by individual persons, and since much secrecy surrounds the operations of some members of the industry, such guesses may be far from accurate. The data obtained by the Tariff Commission, on the other hand, covered 27 of the 30 known manufacturers of graphite products. The three from which no information was obtained were of quite minor significance, and their omission is believed to have no material effect on the results of the canvass.

Before presenting the figures for the two-year period it is of interest to compare the standing of the leading consuming industries in each of the two years separately.

Percentage of total graphite consumed by the leading graphite products, 1923 and 1924

	1923, Per cent	1924, Per cent
1. Facings	43.5	51.5
2. Pigments and paints	16.	18.
3. Crucibles (steel and brass) . .	15.	13.
4. Pencils and crayons	9.	5.
5. Commutator brushes.	8.5	5.
6. Stove polish.	2.5	1.5
7. Lubricants.3/	1.5	1.
8. Miscellaneous	4.	5.
	100.0	100.0

The indicated consumption for 1924 was 32,305 short tons as compared with 39,581 tons in the previous year, showing a reduction of 18 per cent. As compared with other consuming industries, the industries manufacturing foundry facings and paints seem to be more stable. In any event these industries accounted for a larger percentage of the total consumption in the later year when general business was moderately depressed. In other words, the reduction in consumption in the manufacture of these articles was less than it was in other consuming industries.

The average for the two-year period probably furnishes a better idea of the normal rank of the different outlets.

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3 - Lubricants, bearings, bushings, and dashpots combined consumed 3.2 per cent of the total in 1923 and 2.6 per cent in 1924.

Quantity, value, and kind of graphite consumed in the manufacture of various articles

(Annual average for the two-year period 1923-24 as reported to the U. S. Tariff Commission.)

Use	Short tons	Total value	Cents per pound	Total tons, per cent	Form of graphite used
Foundry facings..........	14,279	$ 809,372	2.8	39.7	Amorph. and dust.
Pigments, paints..........	5,065	284,265	2.8	14.1	Amorph. and cryst.
Brass crucibles..........	3,122	346,709	5.6	8.7	Crystalline.
Pencils, crayons..........	2,190	112,365	2.6	6.1	Amorph. and artif.
Commutator brushes..........	2,090	106,263	2.5	5.8	Artif. and amorph.
Steel crucibles..........	1,073	166,318	7.7	3.0	Crystalline.
Stove polish..........	583	32,181	2.8	1.6	Amorphous.
Lubricants..........	451	121,064	13.4	1.3	All.
Bearings, bushings..........	365	100,492	13.8	1.0	No data.
Retorts..........	318	26,380	4.2	.9	Crystalline.
Shot and powder polish..........	100	5,700	2.9	.3	Amorph. and dust.
Packings..........	97	6,365	3.3	.3	Amorph. and cryst.
Ladle stoppers..........	95	9,766	5.1	.3	Crystalline.
Roofing dust..........	87	5,038	2.9	.2	Amorph. and artif.
Dry batteries a/..........	87	5,038	2.9	.2	Amorphous.
Boiler compounds..........	85	8,926	5.2	.2	Crystalline.
Dashpots, plungers..........	68	4,586	3.4	.2	No data.
Electrotype dust..........	47	6,111	6.5	.1	Amorph. and artif.
Electrodes b/..........	38	2,122	2.8	.1	Amorphous.
Finished products..........	30,240	2,159,061	3.6	84.1	Various.
Semifinished(not specified)	5,703	384,377	3.4	15.9	No data.
Total..........	35,943	2,543,438	3.5	100.0	Various.

a/ Obviously incomplete because the chief consumption in this field is of artificial and, in addition, at least two thousand tons of Texas flake are annually consumed in the manufacture of dry batteries.

b/ No data are available on the large quantity of artificial graphite used for electrodes.

Foundry Facings

Foundry facings are employed to give the surface of molding sands a smooth skin, and to enable the castings to be removed freely on cooling. In addition to preventing the sand from sticking to the casting, the facings make it possible to obtain a better surface. As graphite is highly refractory and slippery, it meets these requirements admirably. Occasionally the cheapest grades of graphite are mixed with molding sand itself, but except perhaps in certain parts of Europe the amount so used is trifling. In lieu of graphite, other forms of carbon, such as charcoal, coke, coal and gas retort carbon, may be employed; talc, either alone or mixed with graphite, is another substitute, as are also silica, carborundum and a few other materials. The facings containing graphite or other carbonaceous matter are commonly called "blackings" to distinguish them from "mineral facings" which contain such materials as talc, and silica. Except for the universal requirement of extreme fineness, the preparation of facings follows no generally accepted standard; and the result is that there are probably at least as many formulas as there are manufacturers. Although the foundries almost never manufacture their own facings, a considerable number of foundry supply firms have suitable grinding and mixing equipment. The seven largest facing manufacturers furnish less than one-half the total output, of which the remainder comes from a much larger number of smaller firms.

For green sand molds, foundry facings may be dusted on the surface and then either "slicked" with a tool or the excess may be blown off; sometimes they are applied with a brush. For dry sand work they are applied wet with a swab; molasses water or some similar sticky liquor or clay is commonly added. Nearly all facings require a bonding agent in order to hold the graphite in place against the mold because graphite alone runs before the metal. The proper proportioning of the binder, usually clay, is important.

In addition to being mixed with other constituents in foundry facings, the graphite itself varies largely in purity. According to some authorities a very pure graphite is desirable even when it is to be diluted later with cheaper materials, but others contend that the silica and mica present in lower-grade graphite may be of actual benefit, causing the graphite to cling and to spread better over the surface of the mold. A great deal of dust containing only 40 to 60 per cent carbon is sold by refining mills to the foundry-facing trade, which constitutes virtually the only market for such low-grade material. Amorphous graphite — Korean, Mexican, or domestic — if purchased in crude condition needs to be dried and crushed before undergoing the usual grinding in tube mills, mixing, and air-floating.

Conflicting views exist as to the future of the foundry-facing business. Some feel that the larger employment of sand-blast, welding, and die-casting equipment in foundries will make less necessary the fine finish on the castings that graphite facings are designed to produce, and that this fact will cut down the demand for graphite for this purpose. On the other hand, the sand used for cleaning castings is expensive and the number of castings is steadily increasing.

Pigments and Paints

Even in its thinnest flakes graphite is perfectly opaque; since also it remains unaffected by sulphurous gases, acids, alkalies, and various fumes, it is employed extensively in paints, more particularly in protective paints for structural ironwork. Bridges, railroad cars, smoke stacks, boiler fronts, tanks, metal roofs, and other exposed surfaces, are commonly covered with graphite paint. Graphite invariably must be mixed with other pigments such as iron oxide, lead, or zinc compounds, as otherwise it tends to coagulate in the vehicle and spreads under the brush into an excessively thin coating.[4] Silica or some similar material is also generally necessary to give the requisite tooth--both to enable a thicker film to be applied and to permit repainting. Paints containing too large a percentage of graphite present a satin-like surface which often can not be repainted satisfactorily, for succeeding coats curl up and peel because they can not adhere to the smooth film of graphite.

Both crystalline and amorphous graphites are used extensively in paints. Artificial graphite has also been employed by some manufacturers. Flake graphite has a better covering power than amorphous graphite but there is no demand in the paint trade for the better grades because most of the impurities naturally present in the cheaper grades of graphite, notably silica, actually make it more desirable, for they not only give tooth but also are supposed to add permanence to the paint film. In Michigan and elsewhere graphitic rock is ground directly into pigment, and the product often contains as little as 30 or perhaps only 25 per cent of graphitic carbon. Even after being ground, graphite pigments rarely are worth more than 3½ or 4 cents, and some kinds of amorphous graphite pulverized to pass through 350 mesh sell for $40 a ton (1929). Anthracite coal is sometimes used in these paints.

Crucibles

Graphite crucibles are used in the production of malleable castings, small iron castings, crucible steel, brass and other copper alloys, and zinc castings, and for the melting of gold and silver. The crucibles are divided into two principal groups, (1) steel crucibles and (2) brass crucibles. Other metals are ordinarily melted in one or the other of these two types. The general shape of crucibles is that of an egg cut off flat at both ends. Steel crucibles are barrel-shaped except for the fact that although the bilge comes a little more than halfway up they are often a trifle smaller at the top than at the bottom. In proportion to their height they are generally smaller in diameter than brass crucibles, which differ also in being larger at the top than at the bottom. The notation of size is purely empirical and has been changed several times. Brass crucibles are rated according to capacity, assuming 3 pounds per number; thus a No. 70 crucible, which is a common size, has a capacity of 210 pounds of molten brass.[5] They vary all the way from a No. 12 (36 pounds) to No. 400 (1,200 pounds), and there is a growing tendency to use larger crucibles. Steel crucibles are numbered differently. They are made chiefly in two sizes. A No. 50 pot holds about 95 pounds and a No. 60 about 110 pounds.

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4 - According to Toch ("The Chemistry and Technology of Paints" by M. Toch. 2nd ed., New York, 1916, p. 101.) pure graphite paint will cover from 1,000 to 1,600 square feet to the gallon. The coat looks satisfactory to the eye but is too thin to last long. Although a mixture of silica and graphite produces good results, even it has too much spreading power. On the other hand, a six-year test of a linseed-oil paint containing 75 per cent ferric oxide and 20 per cent silica mixed with 5 per cent of 85 per cent graphite "proved itself to be as good a paint as can be desired for ordinary purposes."

5 - Owing to differences in specific gravity of the various metals and alloys, a No. 70 crucible will melt only 200 pounds of bronze but will melt 250 pounds of silver or 350 pounds of gold.

A different and larger type of graphite crucible is the retort used in the distillation of zinc in silver refineries, in the recovery of secondary zinc from galvanizer's dross, etc. Such retorts are often 40 inches high. Another type of crucible is designed to hold the molten lead or salts used for hardening and tempering small tools, files, etc. Still another is employed for dip-brazing bicycle frames. Numerous special shapes such as those used for annealing boxes and similar services are also made by the crucible manufacturers from the same ingredients that crucibles are made of.

The requisite qualities of a good graphite crucible are refractoriness, mechanical strength, good heat conduction, and long life. Refractoriness and the ability to withstand many heats involve satisfactory resistance to chemical action as well as to high temperatures. The graphite in the wall of a crucible begins to oxidize at a temperature somewhat under 700° C.; its rate of oxidation from the outside varies with the composition of the furnace gases and on the inside with the composition of the material being melted.

Ordinarily approximately 50 per cent of the crucible mixture is graphite, the remainder being chiefly clay and sand or grog. Sometimes the percentage of graphite is much less. The nature of the other ingredients is obviously significant; the clay in particular seems to contribute as much as the graphite to the qualities of the product. Care in manufacture and proper curing vitally affect the serviceability, and the nature of the service and proper handling likewise enter into the final result. So many factors are involved that it is unwise to be too dogmatic about just what does or what does not constitute the best practice in manufacture. The extensive literature that has grown up about this subject is full of conflicting statements out of which may be gleaned only the facts that good clay as well as good graphite must be employed and that proper care must be exercised throughout all the various stages of manufacture including drying, storage, transportation, preheating, handling in the furnace, actual melting service, and cooling between successive heats. If a suitable glaze can be formed on the surface of the crucible, the graphite will be protected from oxidation and thus last longer. As regards practical performance, the following statement by Searle[6] give some information on British practice:

> "It is clearly impossible to give any accurate figures showing how many times a crucible may be used. Some men can use a crucible eighty times or more for cast iron, whilst others can only use a similar crucible half a dozen times. Similarly, in the melting of alloys, steel, and all other purposes for which crucibles are used, the manner in which the tongs fit and the handling of the crucible being much more important than is usually imagined, the following figures represent fair averages:-

For brass,	a crucible should serve	70 to 100 times.
For bronze,	"	about 50 times.
For iron,	"	70 to 90 times.
For steel,	"	6 to 10 times."

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[6] - Searle, A. B., Refractory Materials, Their Manufacture and Uses: London, 1917, pp. 304-25.

Other authorities estimate 60 melts for brass or copper and from 10 to 15 heats for steel.

Kinds of Graphite Used. Various kinds of graphite have been used for making crucibles. Passau (Bohemian) flake was used first, and for inferior crucibles a considerable admixture of amorphous graphite is now used in central Europe, simply because it is cheap. Ceylon plumbago has been universally recognized as the variety best suited for crucible use. American, Canadian, and Madagascar flake have all been used with good success, but there is a wide divergence of opinion as to whether as good crucibles can be made commercially from 100 per cent flake graphite as from the usual mixtures containing a large proportion of Ceylon plumbago. Flake graphite was substituted to a large extent for Ceylon grades during the war, but even France, where Madagascar flake exclusively was used in crucibles during the later years of the war, has slowly reverted to the use of at least a small percentage of Ceylon plumbago. Ceylon graphite has much greater bulk with respect to its surface area, as the individual particles are mostly wedge-shaped or rod-like, and hence it requires proportionately less clay as binder than, for example, the thin flakes of domestic graphite. It is also said to be more nearly free from undesirable impurities such as mica and pyrite. On the other hand, some authorities contend that a large number of thin overlapping flakes is preferable to a smaller number of more or less angular fragments. Although the latter type furnishes a better bond, the former provides better for the slight slip and readjustment within the wall of the crucible as it expands or contracts, and thereby reduces the liability of cracking. Moreover, these flakes, according to tests made by the Bureau of Mines, actually resist oxidation longer, as only the edges are exposed to the oxidizing influences.[7] Abundant evidence has been offered in support of both sides of this question, but the weight of opinion among domestic crucible manufacturers as shown by their purchasing policy is overwhelmingly against employing more than about 25 per cent flake. Most of them prefer to use Ceylong lump or chip for 80 per cent or more of the total graphite admixture. Formerly the remainder was mainly Ceylon dust, but now Madagascar or domestic flake is used instead.

A. V. Bleininger[8] places the comparison on the basis that a dollar's worth of Ceylon graphite yields more crucible value than a dollar's worth of flake, adding that if Ceylon graphite could not be obtained, the production of metal would not be diminished in any way, as "we could get along very well with flake and amorphous graphite, furnace carbon, and coke." He gives the following figures for the actual volume of the different kinds of graphite after thorough shaking:-

	Volume occupied by 100 g., c.c.
Ceylon graphite	90.7
Canadian graphite . . .	119.6
Alabama graphite. . . .	152.0

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7 - Thiessen, R., "Structure of graphite in relation to crucible making:" Jour. Am. Ceramic Soc., July 1919, pp. 508-542.

8 - Bleininger, A. V., Can. Chem. Jour., October, 1918, p. 253.

The specifications for crucible graphite rarely call for much over 90 per cent graphitic carbon, but the nature of the remaining 10 per cent is of much importance. Of the ordinary impurities, mica, which is difficult to remove, is one of the most common and also one of the most injurious; it fuses readily, making pin holes in the wall of the crucible. Carbonates such as limestone are undesirable because they decompose when heated, leaving shrinkage cavities. Sulphur, usually in the form of pyrite, is present in small amount in most Canadian, American, and Bavarian flake and, to a less extent, in Ceylon graphite; only Madagascar flake is virtually free from it. Sulphur is decidedly deleterious, as it not only causes blowholes that may result in a porous condition but also may contaminate the metal that is to be melted.

The size of the graphite particles that go into the crucible mixture is commonly from 20 to 90 mesh; the lower limit of size varies in the specifications of different manufactures from 86-mesh (No. 8 silk bolting cloth) to 125-mesh (No. 12 cloth). Most crucible manufacturers, however, further refine their flake, ordinarily grinding it between buhrstones and then screening out the badly broken flake and dust. This dust, since it is worth but a fraction of the price of good crucible graphite, is kept at a minimum, and manufacturers are reluctant to buy graphite containing too great an excess of gritty impurities that would unduly destroy the particles of graphite. The dust could be disposed of profitably in the form of lubricants, paints, or other finished products, but the amount produced is too small to interest most crucible manufacturers in the production of a diversified line of graphite articles. Most of their fines can be used in stoppers and nozzles which are generally made in the same factories with crucibles.

Production Data. Separate statistics for the production of graphite crucibles are not available. The Federal census reports "crucibles of all kinds, including glasshouse pots, made largely from fire clay and plumbago (graphite)," but these figures cover "miscellaneous products, normally belonging to other industries, made as secondary products by establishments engaged primarily in the manufacture of crucibles." The value of the miscellaneous items was calculated to be only $75,257 in 1925, and, although there are no data for such items in previous years, it may be assumed that the trend of the industry is revealed by the following table:

Production of crucibles, 1919 to 1925
(Data from Federal Census)

	1925	1923	1921	1919
Number of establishments......	11	13	17	22
Wage earners (av. number).....	284	516	412	848
Horsepower....................	1,476	1,647	(a)	2,714
Wages.........................	$ 380,783	$ 626,678	$ 495,973	$ 923,287
Cost of materials.............	$ 754,817	$1,226,159	$ 827,288	$2,233,072
Value of products (b).........	$2,091,518	$3,467,816	$1,969,930	$5,293,688
Value added by manufacture....	$1,336,701	$2,241,657	$1,142,642	$3,060,616

(a) No data.
(b) Does not include crucibles made as secondary products in other establishments.

For 1925, the five establishments in Pennsylvania gave employment to 40 per cent of the wage earners, consumed 56 per cent of the materials, and produced over 57 per cent of the total value of the products. Of the remaining six establishments, two were in New Jersey and one each was in Connecticut, Indiana, Massachusetts, and New York.

The above figures do not cover the large output of crucibles made as secondary products by establishments classified in other industries. The values of such crucibles do not quite follow the same trend as those made as principal products: 1925, $1,869,105; 1923, $809,971; 1921, $564,398; and 1919, $1,570,579. The difference is too slight, however, to alter the general downward tendency.

Imports. Imports of graphite crucibles have been reported separately since the Tariff Act of 1922, but they have been quite small.

Imports for consumption of graphite crucibles, 1922-1928

Calendar year	Number	Value	Unit value
1923	1,655	$ 459	$0.28
1924	- -	- -	- -
1925	3,100	548	0.18
1926	9,513	11,780	1.24
1927	2,583	1,812	0.70
1928	4,170	1,441	0.34

Exports. Exports are of some importance to the industry, as American crucibles are used extensively in Canada, in Mexico, and to a lesser extent in other Latin-America countries. The extent of the export business is not known, however, because the figures for graphite crucibles are included with those of other crucibles. Although the unit values of the graphite crucibles are probably greater than those of other crucibles included in the export classification, the range in sizes and prices of both plumbago and clay crucibles is so great that price alone does not afford a statistical basis for separating the figures. In 1927 the total exports were 558,000 crucibles valued at $108,857. Of these, 356,822, or 64 per cent of the total number, were exported to Mexico. The value of the crucibles exported to Mexico, however, was only $31,286 or 29 per cent of the total value.

Other Graphite Refractories

The refractory properties and other characteristics of graphite that render it desirable for crucibles also its use in a variety of other accessory articles used in smelting and foundry work, such as crucible covers, pouring nozzles, crucible rests and stools, funnel or extension tops, skimmers, phosphorizers, ladle stoppers and stopper sleeves, pyrometer sleeves, furnace bricks and doors, annealing boxes, and case-hardening containers. Special mixtures are used in the so-called "graphite blocks" employed in flattening window glass. Graphite also enters into the composition of certain refractory cements as a lubricant, making them flow more freely under the trowel.

The output of several of these items - notably that of ladle stoppers, which are used at every iron and steel works and at most foundries and brass plants - is large and growing. For some of the articles Ceylon plumbago is used sparingly, if at all, and for a few of them the cheaper grades of domestic graphite such as No. 2 flake may be employed. In general, however, the manufacture of these miscellaneous refractories is undertaken as a branch of the crucible business, and are made by the same firms and from the same materials.

Pencils and Crayons

One of the earliest and by far the best known use of graphite is to make marks on paper. The name "graphite," it may be noted, is derived from the Greek word meaning "to write." In the sixteenth century crayons were being made in England from the graphite found in the Borrowdale mine. For many years solid blocks of the natural material were simply cut into sticks and sold as such. Later they were cut somewhat smaller and protected by a wooden holder, but it was not until late in the 18th century that the present method of making pencil "leads" from an artificial mixture of graphite and clay was adopted. In its early days ownership of the Borrowdale deposit in Cumberland constituted a monopoly of such importance that after a time the government assumed control of the operation. Finally it prohibited the export of this graphite except in the form of pencils. The mine was worked only for a short period -- usually six weeks -- each year, but the product was auctioned weekly on the London black lead market, selling usually for 30 to 40 shillings a pound and choice qualities brought sometimes as much as 140 shillings. Despite all measures for conserving the supply, the richer parts of the mine became exhausted. Poorer portions of the deposit and the great heaps of waste were then picked over and eventually the lean rock was ground and washed, but the material so obtained was of much poorer quality. Various schemes were tried in the effort to bind together the small fragments so as to produce a cake that could be cut up in the same manner as the natural lumps. Most of the available binders proved very unsatisfactory, although some success followed the use of rosin mixed with a little wax or tallow.

In 1795, Conte in France and Hardmuth in Austria both began to make pencils very much in the modern way. The function of the clay is not solely that of a binder. It acts as a vehicle rendering the graphite plastic so that it can be molded readily, and it affords a means of regulating the hardness and of maintaining uniform quality, both of which were impossible with the natural block graphite. Except for the cheaper pencils, a mixture of graphites is generally considered better even than the best single variety. The product of the Borrowdale mine, which was closed in 1833, was exceptionally suitable material; the mineral occurred in pipes, stringers, and nests in association with a dike of altered diorite intruded into volcanic ash.[9] Some of it may still remain, but prospecting in 1878 seemed simply to confirm the fact that this famous deposit was economically exhausted, even tho such little of the product as was obtained was said to have sold then for as much as $10 a pound.

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9 - This statement is from Spence who refers to Mem. Geol. Surv. Great Britain, vol. V. 1916, p. 25, and to Haenig, A., Der Graphite, 1910, p. 41.

Some 15 years after the English mine ceased to operate, similar material was discovered in the Sayan mountains west of Irkutsk in Siberia. This became the well-known Alibert mine which supplied the Faber pencil factory at Nuremburg with all its graphite for many years. After a time, however, this mine likewise was exhausted or abandoned. Since then almost all pencil makers instead of depending upon only one mine have been using two or more entirely different types of graphite, and the results are so satisfactory that the fancy prices formerly paid for the product of these two famous mines could not be obtained again.

Crystalline graphite can not be used alone because it slips over the paper, making only a faint mark; moreover it is difficult to grind it fine enough. However, a particular grade of Ceylon graphite has been used to a considerable extent in blends because it does add smoothness. Bohemian grades have a reputation for blackness, and somewhat more recently the Mexican graphite produced by an American company has found its way into European pencil mixtures and has been used successfully in the United States without much if any admixture of other graphites. In addition to color, freedom from grit, uniformity of grain, and softness are important qualifications for pencil graphite. Artificial graphite, because it often contained small particles of carborundum, was for a long time unpopular with pencil makers, but a certain amount of it is now used for pencils.

Besides graphite and clay, other substances such as sulphide of antimony, lamp black, or finely divided metallic lead may be added. Sometimes the pencil leads are boiled in wax or tallow in order to toughen them or to remove grit. The proportions of the various ingredients vary considerably even for pencils of similar quality. The percentage of graphite is ordinarily higher for soft pencils as the clay tends to make the lead both harder and less lustrous. As a general rule the graphite amounts to 50 per cent or less of the mixture, but it may be considerably more; Cirkel,[10] for example, gives the following recipe as having been employed:

	Parts
Graphite........	30
Clay............	9
Stibnite........	9
Tallow..........	1
	49

and for very hard drawing pencils:

Graphite........	36
Clay............	18
Stibnite........	8
Lampblack.......	2
	64

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[10] - Cirkel, F., Graphite, Its Properties, Occurrence, Refining, and Uses: Canada Dept. of Mines, Mines Branch, 1907, p. 263.

Proper mixing is essential. The clay is carefully selected and washed very thoroughly to eliminate any possible grit, and the mixture is worked and reworked until it can be looped and coiled and even tied into knots. The dough then goes to a hydraulic press and is extruded through holes of the proper size. After being cut to length the leads are packed in a crucible with powdered carbon and burned at a definite temperature (usually 1,500° to 2,000° F.). If heated too rapidly the leads will warp or spring, rendering them useless; they can not even be ground up and reburnt.

The whole process of pencil manufacture is described by Spence as follows:[11]

> "The clay is ground dry, water-floated, and settled in tanks. Graphite and clay are then mixed in the required proportions and further ground between buhrstones in a closed tank. This grinding is wet, and according to the degree of fineness required, lasts from two weeks to three months. The sludge from the buhr mill is then passed to a filter press or vacuum filter, preferably the latter, since the cloth screens of the former tend to clog. The product from the filter is kneaded by hand to the required consistency, and the dough is fed to hydraulic presses which force it, under a pressure of 2,000 pounds per square inch, through dies of the diameter of the finished lead. The lead issues from the die in the form of a continuous string, and the die head, being mounted on a toggle joint, the string is coiled as it exudes from the die and is caught in a shallow metal dish. The dish is removed when full, and the lead is uncoiled by hand and pinched off into lengths, each equal to three pencil lengths. At this stage, the material is quite tough and pliable and can be readily handled without breaking or deformation. The lengths of lead are laid between boards and allowed to air dry, after which they are cut by hand into pencil lengths and arranged in bundles in graphite crucibles or boxes. They are then placed in a kiln and baked for several hours at a temperature of 1,500° to 2,000° F., after which they are ready to be placed in the wood casings. An intermediate drying may take place before the final baking, and is effected in iron boxes in a hot air chamber having a temperature of about 150° F.
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> "The wood casings consist of cedar blocks, grooved to receive the leads, and measuring 7¼" x 2¼" x 3-3/16." Each block is provided with six grooves and after insertion of the leads, the blocks are dipped in glue and clamped together in bundles of a dozen or less, and allowed to dry. Finally, the glued blocks are cut up into individual pencils, which are then trimmed, sandpapered, painted, varnished, and stamped.

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[11] - Spence, H. S., op. cit., pp. 146-7.

> "To impart the necessary strength, the softer grades of pencils have leads of greater diameter than the harder grades, in which the larger proportion of clay used serves the same purpose."

The value of pencils manufactured in the United States first exceeded $1,000,000 in the year 1890. Although the domestic industry continued to grow quite rapidly, pencils, particularly drawing pencils of the better quality, were imported into the United States in large quantities before the war, principally from Germany and Austria. When supplies from foreign sources were largely cut off by the outbreak of hostilities, the American industry expanded rapidly. The Armistice found it in very favorable condition. While the imports have recovered to the point where their value amounts to $600,000 to $700,000 annually, or practically the same as pre-war figures, exports have grown to more than three times the imports and domestic business has increased to very large proportions. The American pencil industry having outstripped that of Czechoslovakia, has now become larger than that of any other country, with the possible exception of Germany.[12] A large part of the increased business of American pencil manufacturers, both in domestic and export markets, is the result of the extensive use of automatic magazine pencils.

With respect to raw materials the American pencil industry is well-situated. Previous to 1900 it used Bavarian or Bohemian graphite and German clay, but later it began to use Mexican graphite and, when the necessity arose, domestic clay. For a time after the war, it derived practically all its raw materials from the North American continent, but one or more manufacturers have since reverted to the use of Klingenberg clay. For the better pencils cedar wood is preferred and even foreign manufacturers draw their supplies of such wood chiefly from the southern United States.

The American pencil industry, which is centered mainly in Illinois, New Jersey, New York, and Pennsylvania, produces annually, according to recent figures of the Federal Census, products valued at approximately $25,000,000. A little more than one-half of this total represents wooden pencils and about $1,000,000 annually represents pencil leads for use in mechanical pencils.

Commutator Brushes

Carbon or graphite brushes have largely displaced metal brushes for electric generators and motors because, due to their being harder and having more electrical resistance, they provide a better contact and otherwise reduce sparking. With metal brushes it is difficult to keep the surface of the commutator smooth, as it does not wear down evenly. Graphite is used in most varieties of brushes, but it is usually mixed with other ingredients. Numerous grades are on the market which are composed wholly of graphite and little binding material, but they have very limited application. Coke, lamp black, or metal powders such as bronze, brass or copper are mixed with a graphite in varying proportions. Metal gauze brushes filled with graphite were used formerly, but they have been largely superseded by metal graphite brushes in which the metal enters in the form of powder. These various mixtures after being made up in their proper proportions are molded under high pressure and baked to carbonize the binder. Sometimes they are electroplated and the larger ones may have a "pig tail" soldered or bolted to them.

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[12] - European manufacturers, however, have regained much of the business they lost during the war when Japan and the United States were the leading exporters.

In the United States amorphous and artificial graphite are employed, but certain foreign brushes are said to contain Ceylon or flake graphite ground to 100 mesh.

Graphite is added to electrical brushes for its lubricating and conducting properties. The ordinary carbon brush contains very little graphite and is composed mainly of amorphous carbon, usually petroleum coke. Ordinarily the brushes are impregnated with some additional lubricant in the form of grease in order to cut down abrasion, reduce friction, and create a little higher contact resistance, thereby improving the commutating properties. The carbon brush is medium hard and being moderately cheap is considered a good general-purpose brush. Brushes containing a somewhat larger proportion of graphite and less coke are known as graphite-carbon brushes. Such brushes are self-lubricating and moderately soft, but while they have a high current-carrying capacity, the contact drop and hence the commutating properties are not entirely satisfactory. This type of brush is used extensively on industrial motors, railway and mining motors, and on moderate speed generators; special grades are employed for light service, such as for magnetos and fan motors of both direct current and universal types. Graphite brushes are soft and have little mechanical strength, but being nonabrasive they are much favored for service requiring quiet operation. They may be used in high-speed work, automobiles, lighting generators, electric vehicle and battery locomotive motors, battery-charging and other low-voltage generators, in slip ring machines, and occasionally as lubricating brushes on electroplating generators.[13] Electrographitic or graphitized carbon brushes, made in electric furnaces at extremely high temperatures from petroleum coke or other forms of amorphous carbon, are suitable for a variety of uses. Metal graphite brushes are used extensively in automobile starters, plating generators, and railroad signal motors, as well as for slip ring machines of large power.

Stove Polish

Amorphous graphite, chiefly Korean and Mexican, is used in stove polishes. Carbon black may be added to improve the color, particularly if impure grades are used. Clay, rosin, soap, or asphalt may be used as a binder for the cake polishes; for the liquid polishes, gasoline, various oils, ammonia, or a plain water are used as vehicles. In all cases the graphite has to be ground fine.

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13 - Kalb, W. C., "Application of brushes to electrical machinery:" Power, vol. 49, No. 7, Feb. 18, 1919, p. 241.

Lubricants

Graphite is an excellent lubricant and retains its lubricating properties at all temperatures and under conditions that cause oil or grease to decompose or lose body. It adheres readily to metal and not only fills up the pores but also forms a protective film which can not be squeezed out even at high bearing pressures. The field for solid lubricants has increased rapidly in late years due to the increased use of heavy machinery. While mica, talc, sulphur and other substances are used for similar purposes, graphite is by far the most widely used and in many cases the best solid lubricant. The total tonnage of graphite used in lubricants, however, is quite small.

According to Spence:-[14]

> "For ordinary lubricating purposes in loose, open bearings, gears, slides, etc., graphite is commonly mixed with oil or grease, and there are a variety of such compounds on the market, many of them designed for work under special conditions, such as exposure to salt water, acids or alkalies, in dredges, pump plungers, winches, mining machinery, etc., or at different temperatures, where varying degrees of viscosity are required.
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> "In cylinder lubrication for steam and gas engines, compressors, etc., modern practice is to feed dry flake or powdered graphite in addition to grease or oil. For this purpose, numerous special lubricators have been devised. In marine engines, the use of graphite for cylinder lubrication is especially advantageous, as by its use, the amount of oil finding its way into the condensers and boilers is materially reduced.
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> "Graphite is also used in pipe joint compounds, for lubricating and sealing the threads and flanges of steam, water, gas, oil and air pipes, and for bolts, nuts, studs, caps, boiler plugs, manhole plates of boilers, gas retort doors, metal gaskets, etc. Such compounds replace, and are claimed to be superior to, red or white lead. As in the case of graphite paints, superior merit is claimed for each of the three types of graphite -- natural flake and artificial and natural amorphous -- for use in lubricating oils and greases.
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> "Dry graphite powder is used for lubricating the actions and bridges of pianos and organs, and in short, any wooden or other surface when the use of oil or grease might be detrimental, such as in textile machines. It is employed, also, in typesetting machines, to give the space bands, channel plates, etc., a dry, smooth surface.

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14 - Spence, H. S., op. cit. pp. 155-6.

> "To minimize water friction, yacht and launch bottoms are sometimes dusted with graphite after a preliminary light coat of varnish or shellac has been applied, and when dry, are polished with cloths or waste. The graphite used for this purpose is sometimes termed 'potlead.'"

Various so-called self-lubricating bearings and bushings are on the market. Some of them are hardwood impregnated with a lubricating compound containing graphite. Another type is a bronze casting having grooves or slots filled with a graphite mixture and then baked and afterwards broached to the proper size. The former are used extensively for light duty parts -- for shackle pins in automobiles and for loose pulleys and bearings on light textile machinery. The latter are especially adapted to the requirements of trolley wheel and windmill bushings and to other moderately heavy service in places difficult of access where lubrication by ordinary means might be neglected. Antifriction alloys into which graphite is incorporated during the melt have been produced but do not seems to have worked well. Practically pure graphite consolidated under a pressure of 20 tons per square inch is offered in various forms under the name of "morganite" by the Morgan Crucible Co. of London, England. Bearings machined from this material are claimed to be mechanically strong and possessed of the lowest possible coefficient of friction.

Oildag, the well known lubricating compound, of the Acheson Graphite Co. is a colloidal suspension in oil of deflocculated graphite said to be "graphite reduced to the molecular form, the finest state of subdivision" (by a chemical process using tannic acid).

The lubricating qualities of graphite result in its employment in various packings, particularly for steam engines and pumps. Plungers made of graphite or graphite-impregnated metal are used in pneumatic tube service equipment in stores, in dashpots used in electric train equipment, in the dashpots of arc lamps, and for other apparatus of this general nature where it is necessary to have plungers lubricated but where it is not desirable to use oil. Efforts are being made to market a very pure (99+%) natural graphite for lubricating automobile engines; the finely powdered material can be introduced directly into the cylinders through the carburetor.

Graphite Electrodes

The production of electrodes has been increasing rapidly with the rapid expansion in the use of electric furnace and electrolytic processes. Electrodes are of two principal types -- graphite and amorphous. There are two types of amorphous electrodes -- petroleum coke and anthracite. The domestic production of all classes was estimated by the U. S. Tariff Commission in 1921 as amounting to $10,000,000 or more annually. Although a tonnage business, the electrode manufacturing industry is one requiring careful control and constant inspection.

Coke electrodes are employed principally in the manufacture of aluminum. Anthracite electrodes are used principally in the production of electric steel, ferroalloys, calcium carbide, and similar electric furnace products.

The graphite electrodes, used chiefly in the electrolytic industries (notably the manufacture of chlorine and caustic soda) and in small and medium sized electric furnaces, are not made from natural graphite. They are more properly called graphitized electrodes. Attempts to produce satisfactory electrodes out of powdered graphite and a binder have generally failed. Tar and other binding agents have been employed, but electrodes made in this manner lack sufficient strength and soon break.

The three types of electrodes differ in their properties and, therefore, one type can not ordinarily be substituted for another. The properties which must be considered in choosing the proper electrode include the following: Specific gravity, mechanical strength, hardness, density, sonority, electrical and thermal conductivity, the purity and the nature of the ash produced.

Carbon electrodes are made from some form of carbon mixed with tar or pitch, molded and finally baked to drive off volatile matter. Retort carbon and petroleum coke have been largely used and are still employed wherever the purity of the electrode is important as in the manufacture of aluminum which, since it requires a larger consumption per unit of product than any other large use, requires an electrode that will yield little or no ash but that will contaminate the product. For most electrical smelting where mechanical strength, electrical conductivity, and cheapness are more essential than extreme purity, anthracite is now generally used. Graphitized electrodes are relatively pure, have good conductivity, and resist oxidation better than other types. They have the further advantage that they can be machined. In size they range from one-sixteenth inch to 12 inches or more in diameter.

Dry Batteries

Graphite is mixed with the manganese-dioxide in dry batteries to give conductivity. Granulated carbon was formerly used for this purpose, but as graphite is a much better conductor it has largely displaced amorphous forms of carbon for this purpose. Partly for this reason but more particularly because of the enormous increase in the number of dry cells produced, the dry battery industry, formerly an almost insignificant factor in consumption of graphite, has recently become one of the leading outlets. In 1928 it appears to have absorbed 50 to 75 per cent of its domestic output of crystalline flake, a much greater quantity of artificial graphite, and also a little amorphous graphite. For 10 years before the war, the Census figures showed an increase in domestic production from less than 5 million in 1904 to over 71 million in 1914. These figures appear insignificant, however, in comparison with enormous advances made since 1920. In 1927, the number of dry cells (including 6-inch radio B and C, and flashlight batteries) reported by the Census was 718,641,735 and the value of the products (including certain parts and supplies) was $48,986,860.

The use of amorphous seems to be on the decline, being displaced by more expensive varieties. For this purpose Texas flake seems to be much superior to Alabama flake, but it has to compete with artificial graphite which is said to be equally suitable. The largest producer of dry cells now controls the domestic production of artificial graphite. Very little foreign graphite is used in dry cells.

Miscellaneous Uses

Electrotyping graphite is very finely powdered, and is ordinarily made from either very pure amorphous dust or artificial graphite. This graphite is used in two ways. First it is dusted upon the forms which are polished so that the wax mold can be stripped clean, and then it is used once more for covering the mold, so as to form a conducting surface when immersed in the plating bath. In boiler compounds crystalline graphite acts as a lubricant, working its way into the scale and loosening it and preventing new scale from adhering to the metal. Either as a lubricant or simply as a filler it enters into steam and engine packings, hard rubber compositions, hemp rope, wire rope and cable, rubber valve discs and washers, etc. It is used as a dusting agent on certain kinds of prepared roofing to prevent sticking. The polishing of shot and the glazing of black and smokeless powder require a substantial amount of amorphous or dust graphite. One of the functions of the graphite used with explosives is to act as a lubricant, permitting the grains of explosive to flow freely without danger of spontaneous ignition. A somewhat similar use is for treating tea leaves and coffee beans. The graphite film is harmless and it protects the products from moisture and improves their color and general appearance.

GRAPHITE SUBSTITUTES

Because of its employment in crucibles used for melting many of the metals needed for the manufacture of munitions, graphite has been considered an essential war mineral and it fills an important place in the peacetime life of the nation. For almost all of its applications, except in crucible manufacture, substitutes can be found for graphite, many of which are quite as good and almost as cheap. Even the use of crystalline graphite in crucibles can be avoided by melting in electric furnaces, and, as has been noted elsewhere, the trend has been rapidly in that direction. Crucibles themselves can be made with various proportions of graphite or wholly without it; also, instead of the widely preferred Ceylon lump, flake graphite can be substituted with little if any detriment, and in Central Europe fairly good crucibles have been made for centuries with amorphous graphite. In general, then, the use of a particular kind of graphite for a particular purpose is mainly a matter of convenience and price. From a practical standpoint this statement may appear to be too strong, but the facts are nevertheless essentially true. This becomes apparent if we analyze the principal uses one by one.

Graphite dustings can be at once dismissed from consideration because substitutes such as scrap mica and talc, which are both abundant and cheap, may be freely used therefor. These same two minerals compete even now with graphite in lubricants, and for most lubricating purposes ordinary oils and greases can be used almost as well. For steam packings, use is made of asbestos, rubber, and other materials with suitable lubricants, and for boiler compounds graphite now competes on terms of practical equality with a rather large variety of chemical preparations. In pigments and paints, lampblack gives as good or better color than graphite, and various combinations are made up that duplicate any of the other useful properties of graphite as a paint material.

Numerous other preparations besides graphite are on the market for use in foundry facings, now by far the largest application of graphite. With the possible exception of certain silica-molasses facings most of these other preparations have a much more limited use. Without in any way seeming to detract from the excellent reputation of the various graphite facings, it can be admitted that, if need arose, foundries could wholly dispense with the use of graphite without injuring the quality of their castings or very substantially increasing their costs.

For most of these uses even the size of the particle is not of prime importance. It should be remembered that much of the finely ground crystalline graphite such as that used in foundry facings, to take only one example, is essentially a by-product of the production of crystalline flake for making crucibles or refractories. For most of such uses natural amorphous or artificially manufactured graphite would serve quite as well.

The statement has frequently been made that no satisfactory substitute for crystalline graphite in the manufacture of crucibles has been found. It has even been asserted more specifically that Ceylon plumbago is essential to the effective operation of munition factories even during a war emergency when price is not the major consideration. The experience of Germany during the Great War bears upon this question.

Normally Germany imported about 70 per cent of its graphite supply; part of this amount, however, was used for producing items which - like stove polish, paints, and pencils -- were not needed in such great quantities in war time. A shortage of graphite developed, but home production was increased by introducing better methods at the Bavarian mines (most of which had been operated in a small way by lessees) and imports from Austria Hungary were maintained. Bavarian graphite was found suitable for making crucibles and replaced the lump material formerly imported from Ceylon and Siberia. One method for rendering the small Passau flake more refractory and thus better suited for crucible use was to press it into larger aggregates, similar to briquets. Arrangements were made for turning over all used crucibles to manufacturers, who extracted the graphite so that it could be used over again; for this purpose hydrofluoric acid was often employed. Graphite for lubricating purposes was obtained from kish collected at ferro-silicon furnaces iron and steel works, and caustic soda plants.

The various measures for increasing supplies of graphite were supplemented by measures for reducing consumption. The principal savings resulted from the adoption of methods of melting that did not require crucibles. The use of crucibles was restricted to the melting of pure aluminum, pure zinc, silver and gold, copper and copper alloys, hard solders, and special steels. Numerous graphite substitutes containing 39 to 77 per cent carbon were found satisfactory for foundry facings and other purposes, although since many of them contained as much as 1 per cent sulphur, they had to be used with caution. In May, 1917, a laboratory was added to the Graphit-Vermittlungstelle for the purpose of developing economies in the use of crucibles and fostering the use of substitutes for graphite. This agency, originally formed under the auspices of the association of German iron foundries, was eventually given complete control of all graphite distribution and trade throughout the country.

In the United States and the Allied countries the shortage of graphite during the World War never became acute. Expansion in domestic output of both natural and artificial graphite more than sufficed to take care of increased American needs. The War Trade Board recommended the employment of 20 per cent and eventually 25 per cent of domestic flake in the manufacture of crucibles, but this was largely for the purpose of conserving shipping space and because of the length of time required for shipments to be made from Ceylon and Madagascar.[15]

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[15] - The increased production during the war, it should be noted, was accomplished only because of largely increased prices.